Inverted Ligand Field Theory

Literature Group Meeting
Grayson Ritch
June 8, 2018
**d-Block Metals**

![Periodic Table of Elements](image_url)
**d-Block Metals**

- Valance orbitals are *d*-orbitals
- 5 degenerate *d*-orbitals that can hold 2e⁻ each for a total of 10e⁻
- *d*-orbitals differ in their 3-D orientation
The d-orbitals

- 5 degenerate (same energy) orbitals in the absence of a ligand environment

- Introduction of a ligand field perturbs the energy of each orbital differently depending on the geometry of the ligand field
Crystal Field Splitting

Strong interaction with ligands

Moderate interaction with ligands

Weak interaction with ligands

dx^2-y^2

dxy

dxz
dyz
dz^2

No ligand field

Square planar ligand field
A Few Common Splitting Patterns

Crystal field diagrams can be derived for various different complex geometries in a similar manner.
Ligand Field Theory

- Ligands are not point charges!

- Combinations of ligand orbitals combine with metal orbitals to make a part of bonding and anti-bonding molecular orbitals

- The symmetry and energy of these different combination of ligand orbitals dictate which d-orbitals they combine with

- We can derive a the same splitting of the d-orbitals we obtained via crystal field theory
Polarization of Molecular Orbitals

Atomic orbitals are equal in energy

- Both bonding and anti-bonding molecular orbitals have an equal contribution from each atomic orbital

Examples

- $H_2$  $O_2$
- $N_2$  $Cl_2$

Atomic orbitals are unequal in energy

- Bonding molecular orbitals have a greater contribution from the lower energy atomic orbitals
- Anti-bonding orbitals have a greater contribution from the higher energy atomic orbitals

Examples

- $HCl$  $CN^-$
- $CO$  $NO$

Reactivity of compounds is dependent on the polarization of their molecular orbitals
Inverted Ligand Field

Normal Square Planar Ligand Field Diagram

Note the assumption is that the metal orbitals are higher in energy than the ligand orbitals.
An inverted ligand field arises when the energy of the ligand orbitals are higher in energy than the metal $d$-orbitals.
Characteristics of an inverted ligand field

Inverted Square Planar Ligand Field Diagram

- The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is ligand based rather than metal based.
  - Suggests reactivity of such complexes might be more dependent on the ligands than the metal orbitals.

- The metal is essentially in a d^{10} electronic configuration.
  - To quote Nate, “They’re dope.”
What causes an inverted ligand field?

Inverted Square Planar Ligand Field Diagram

- Highly electronegative ligands increase the energy of the ligand orbitals
- High oxidation state of metal help lower the energy of the metal d-orbitals
Cu(CF₃)₄ as an example of invert ligand field

- Formally a 16e⁻ Cu(III) complex
- Geometry is roughly square planar with some distortions due to the size of the CF₃ ligands
- Remarkably stable for a Cu(III) complex
Some History

Synder presented a conversional theoretical paper 1995 describing a formally Cu(III)(CF₃)₄⁻ salt as Cu(I) complex with oxidation occurring on the CF₃ ligands rather than the metal center.

\[
\text{CF}_3 \quad \text{CF}_3^- \\
\text{F}_3\text{C}^- \quad \text{Cu}^+ \quad \text{CF}_3 \\
\text{CF}_3^- \\
\text{CF}_3^+
\]

The copper atom was calculated to have a partial charge of +0.71, each carbon has a charge of +0.74, and each fluorine -0.39.

The 4 CF₃ units were calculated to contain 25.4 electrons each which is the average of 3 CF₃⁻ and 1 CF₃⁺.

Academic Fisticuffs

Formal Oxidation State versus Partial Charge—A Comment

Martin Kaupp* and Hans Georg von Schnering

“Evidently, there must be a gross misunderstanding. Snyder has confused two important but fundamentally different concepts: the formal oxidation state, and partial charges as obtained, for example, from population analyses.”


Distinguishing Copper d⁸ and d¹⁰ Configurations in a Highly Ionic Complex;
A Nonformal Metal Oxidation State

James P. Snyder*

“Since Pauling’s introduction of the concept over 40 years ago assignment of formal oxidation numbers and oxidation states has proved to be useful for teaching elementary chemical concepts and for cataloguing trends in the periodic table. Nonetheless, apart from isolated monoatomic ions, designation of a formal oxidation state is entirely arbitrary and often accompanied by assumptions as underscored by Kaupp and vonSchnering.”

Evidence for inverted Ligand field

Inverted Ligand Field Diagrams for $T_d$ and $D_{4h}$

For an inverted ligand field $D_{4h}$ geometry is energetically favorable by $4/3 e_\sigma$ for a 16 electron system

K.M. Lancaster et al., JACS, 2016, 138, 1922-31
Evidence for inverted Ligand field

UV-vis

Cu(CF₃)₄⁻

Large MLCT
(predicted $\varepsilon > 20\,000\text{M}^{-1}\text{cm}^{-1}$)

No d-d transitions
(predicted $\varepsilon = 100\text{M}^{-1}\text{cm}^{-1}$)

- no observed d-d transitions expected for a D₄h d⁸ metal
- having the d-d transition buried under the charge transfer band suggest an very high value for the crystal field splitting

K.M. Lancaster et al., JACS, 2016, 138, 1922-31
Evidence for inverted Ligand field

Cu K-edge XAS

- Use of Cu 1s_{2p} RIXS to assign the peak at 8981eV assigned to a Cu 1s $\rightarrow$ CF$_3$ $\sigma^*$ transition

- Lack of several spectroscopic features, L$_{2,3}$-satellite features, that arise from p-d and d-d electron transitions suggest a d$_{10}$ electronic configuration

K.M. Lancaster et al., JACS, 2016, 138, 1922-31
Inverted Ligand Field as a function of Oxidation state

Red is for predominately metal based orbitals
Blue is for predominately ligand based orbitals

Inverted ligand field present with the Cu(II) and (III) structures but not for Cu(I)

S. Alvarez et al., Chem. Rev., 2016, 116, 8173-8192
Theoretical Reactivity of Cu(CF$_3$)$_4$

Thermodynamically unfavorable to abstract a CF$_3^+$ with PH$_3$ by +47 kcal/mol with a kinetic barrier of +79 kcal

Thermodynamically favorable to abstract a CF$_3^+$ with F by -26 kcal/mol with a kinetic barrier of +56 kcal

“Even if the latter potentially requires drastic thermal conditions to be observed, we are not deterred; computational attempts to lower this reaction barrier, with different substituents, are in progress.”

S. Alvarez et al., Chem. Rev., 2016, 116, 8173-8192
Conclusions

Inverted ligand field theory suggests an alternative explanation for the spectroscopic properties and chemical reactivity of many high valent metal complexes

Requires the ligand orbitals to be higher in energy than the metal $d$ orbitals
- Most common for high valent metals
- Typical ligands: CF$_3$, F

The unique reactivity of these proposed inverted field compounds is underexplored